

Effects of Stone-Wales Defect on Adsorption & Insertion Capacity of Nanotubes

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ABSTRACT

Stone-Wales defect (a dipole of a 5-7 ring pair) is one of the most important defective structures in carbon nanotubes. Using a bond order potential combined with molecular dynamics, we found that this defect could form thermally at high temperature. A first-principles discrete variational method was applied to calculate the interactions of a Stone-Wales defect with foreign atoms such as H, B, C, N, O, F, Si, P, Li and Na. The results show that, adsorption of these atoms to heptagonal center is energetically preferred when compared with pentagonal or hexagonal centers. For defect free tubes, cohesive energies of H, C, N, O, F and P are positive or near zero, which indicates it would be difficult to bind these atoms to the wall of nanotubes. The presence of Stone-Wales defects is beneficial to the adsorption capacity of B, N, F, and Si among the 10 foreign atoms studied. Also, this defect can significantly reduce the resistant force of atom insertion through tube walls.

Keywords: Carbon Nanotubes; Adsorption; Defects; First-principles calculation.

1 INTRODUCTION

As more experimental results become available and theoretical investigations get deeper with time, carbon nanotubes (CNTs) are found to be not as perfect as they seem. Defects such as non-hexagonal rings, impurity and incomplete bonds may present in as-prepared CNTs [1,2]. The defective structures in the CNTs modify the hexagonal network of carbon-carbon bonds, and therefore, may affect the adsorption capacity of foreign atoms on CNTs. On the other hand, many potential applications of CNTs may rely on this adsorption capacity. One example is hydrogen storage that was once believed to be one of the most promising applications, but recent studies indicate that this was over-optimistic [3]. Adsorption of hydrogen seems most likely due to metal impurities in as-prepared CNTs, not due to CNTs themselves. Efforts to produce highly defective CNTs may be a way to overcome this problem because defective structures may promote the adsorption of metal particles and hydrogen. A similar situation is also found in the application of CNTs as a mechanical reinforcement in composites. Weak bonding between

CNTs and a polymer matrix has been observed [4]. The presence of high-density defects can change the properties of the tube wall, and may therefore also change the interface adhesive properties. The common question raised is, how foreign atoms interact with defective structures on CNTs. This work uses a first-principle method to study the interaction of a Stone-Wales defect [5,6] with foreign atoms.

2 MODELING AND METHODOLOGY

The Stone-Wales defect is one of the most important defective structures in CNTs. Thrower pointed out a possible 5-7 ring defect in graphite [7]. Stone and Wales showed that a dipole consisting of a pair of 5-7 rings can be created by rotating a C-C bond in the hexagonal network by 90° [8]. Such a dipole was later called a Stone-Wales defect [5,6]. The reason to select the Stone-Wales defects as the current study object is that the defect has a simple structure, and possesses relative low formation energy. Fig.1 shows a result of our molecular dynamics (MD) simulations on a (20,20) carbon nanotube using a bond order potential [9]. The initial defect-free structure was annealed at 5000 K for 25 ps, and then relaxed to an equilibrium state. It can be seen that the Stone-Wales defects are the only defects in this case.

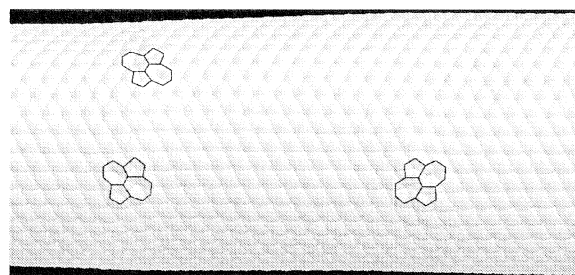


Fig.1. Stone-Wales defects in a (20,20) single-walled CNT generated at 5000 K.

2.1 Cluster model

The cluster model used in the current calculation consists of 81 atoms, 80 of them are carbon atoms forming a graphene sheet, and one foreign atom. Two types of

current calculation, the effect due to wall-bending of CNTs has been neglected. The foreign atom is placed over the sheet at the symmetrical positions, i.e, over a carbon atom, or over a bond, or over the center of a ring.

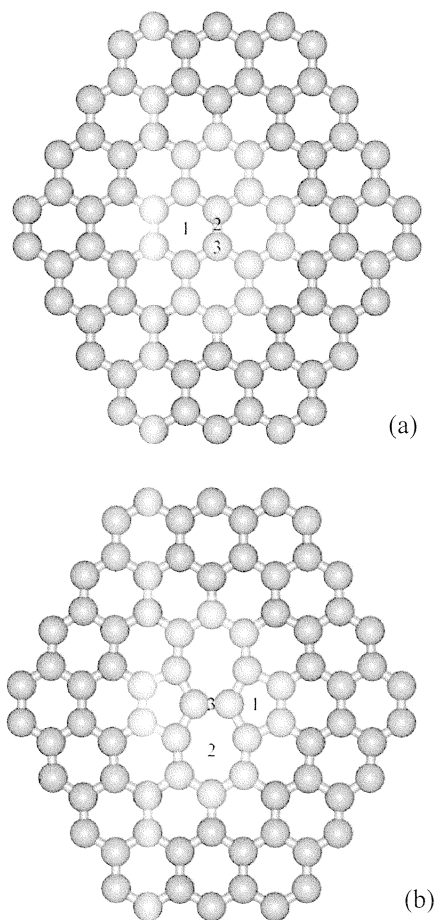


Fig.2. Model clusters: (a) defect free, (b) Stone-Wales defect. Number 1, 2 and 3 in (a) is corresponding to the positions of over-ring, over-bond and over-atom, respectively.

2.2 Methodology

The theoretical calculation adopts the first-principles discrete variational method [10] in which the molecular eigenfunctions are obtained by linear combinations of atom orbitals (LCAO). These orbitals are obtained by numerically solving the Hartree-Fock equation for a free atom with a set of discrete sample points. The non-local exchange-correlation operator of the Hartree-Fock equation is approximated by a local exchange-correlation Barth-Hedin potential [11]. Matrix elements of the Hamiltonian and the overlap operator are calculated by three-dimensional Diophantine numerical integration. The convergence criterion is chosen such that the difference between two consecutive values of the charge self-

consistent integration is less than 10^{-4} . The model was validated by comparing our calculation results on the binding energy of a carbon atom within the graphene sheet as well as on the formation energy of a Stone-Wales defect against other experimental and theoretical data in the literature [12,13].

3 RESULTS AND DISCUSSION

A total of 10 different foreign atoms have been considered. They are H, B, C, N, O, F, Si, P, Li and Na. The binding energy of a foreign atom to a CNT at a distance R can be calculated by

$$E_{\text{bin}}(R) = E_{\text{tot}}^{\text{Cluster}}(R) - E_{\text{tot}}^{\text{sheet}} - E_{\text{tot}}^{\text{Impurity}}$$

where $E_{\text{tot}}^{\text{Cluster}}$ is the total energy of the cluster, including all 81 atoms; and $E_{\text{tot}}^{\text{sheet}}$ is the total energy of the 80 carbon atoms in the sheet only; $E_{\text{tot}}^{\text{Impurity}}$ is the total energy of the foreign atom at the free state. By changing the value of R in small steps, we may obtain the function $E_{\text{bin}}(R)$. Fig.3(a)

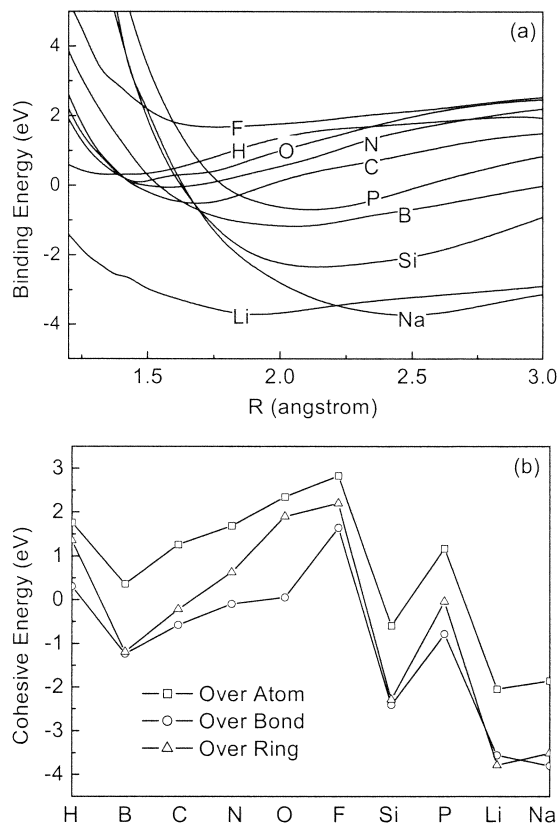


Fig.3. (a) Binding energies at over-bond position in a defect-free cluster. (b) Cohesive energy at different positions in a defect-free cluster.

shows the binding energy of foreign atoms placed at the over-bond position in a defect-free cluster. The cohesive energy of foreign atoms in Fig.3(b) corresponds to the minimum binding energy in each position.

The cohesive energy is the key indicator of the absorbing tendency of a foreign atom to the wall of CNTs. It is found that the binding energy of foreign atoms at an over-atom position is always higher than that at over-bond and over-ring positions. H and F always have positive cohesive energies to CNTs, which indicates that external forces are required for the adsorption of H or F on CNTs. This could be one of the reasons for the difficulty of hydrogen storage in CNTs. From boron to fluorine, the cohesive energy increases as the numbers of p electrons increase. From this point of view, the carbon nanotube with sp² hybridization is chemically stable. Li and Na atoms possess quite low cohesive energy; therefore they are expected to be absorbed on CNTs easily. A high storage capacity of Li has been reported in single-walled CNTs [14].

With the introduction of a Stone-Wales defect in CNTs, additional pentagonal and heptagonal rings have been created. A comparison of cohesive energy for atoms placed

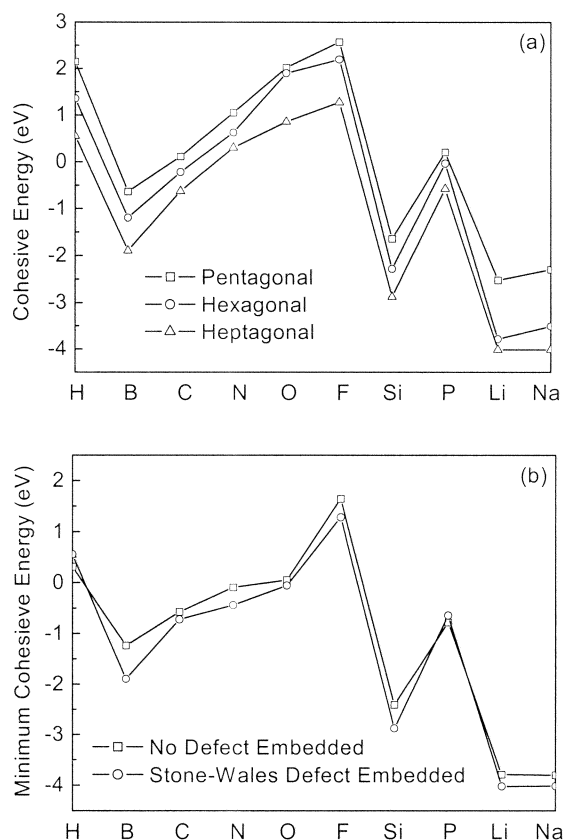


Fig.4. (a) Comparison of cohesive energy of foreign atoms absorbed by rings of pentagon, hexagon and heptagon. (b) Comparison of minimum cohesive energy of foreign atoms to CNTs with and without a Stone-Wales defect.

over different types of rings is shown in Fig.4(a). It is observed that the foreign atoms generally prefer to locate at the center of the heptagon. For a defect-free nanotube (hexagon rings only), the common elements in polymers such as H, C, N, O, F and P have a positive or near zero cohesive energy, which implies weak bonding if carbon nanotubes are embedded in polymers. This has been observed by our recent experiments on CNT reinforced composites [4]. The presence of a heptagon reduces the binding energy by about 0.5 eV for some foreign atoms, which would therefore be beneficial for adsorption.

In order to make a comparison between a defect-free CNT and a CNT with a Stone-Wales defect, we select the lowest cohesive energy for all three positions and present the results in Fig.4(b). It is found that, the introduction of Stone-Wales defects would only benefit the adsorption capacity of B, N, F, and Si among the 10 foreign atoms studied.

Doping atoms into tubule is another possible way to modify the properties of CNTs. The routine for a foreign atom accessing into the tubule can be via open ends or defect structures on the tube wall. Fig.5(a) shows the energy barrier of Na atoms passing through the tube wall.

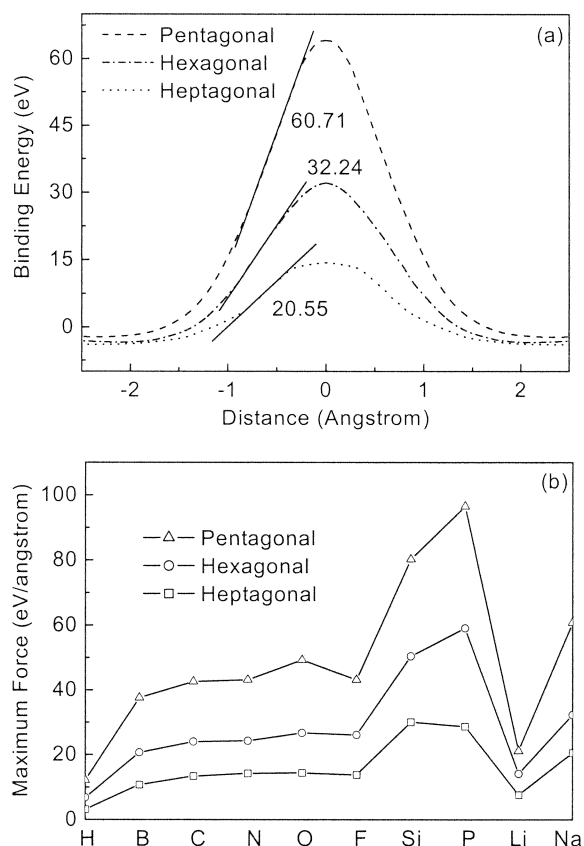


Fig.5. (a) Energy barrier for inserting a Na atoms through the wall of a CNT. The unit of maximum resistant forces denoted in the figure is eV/Å. (b) The maximum resistant force of atom insertion through tube wall.

The forces required to insert the atom were estimated from the steepest slope in the curves. As denoted in Fig.5(a), pushing a Na atom through pentagonal, hexagonal and heptagonal rings on the wall, the maximum resistant forces are 60.71, 32.24 and 20.55 eV/Å respectively. It indicates that the presence of Stone-Wales defects significantly reduce the resistant force. Fig.5(b) shows the forces of all 10 elements we have studied. It reveals that, H and Li atoms, which are the elements expected to be used in energy storage applications, can pass through Stone-Wales defect at relatively low resistant levels.

4 CONCLUSIONS

First-principles discrete variational method has been applied to study the interactions of Stone-Wales defects in carbon nanotube with foreign atoms of H, B, C, N, O, F, Si, P, Li and Na. Our simulations show that:

(1) Adsorption of these foreign atoms to heptagonal center is energetically preferred when compared with pentagonal or hexagonal centers.

(2) For defect free tubes, cohesive energy of H, C, N, O, F and P is positive or near zero, which indicates it would be difficult to bind these atoms to the wall of tubes.

(3) Presence of Stone-Wales defects is found to be beneficial to the adsorption capacity of B, N, F, and Si among the 10 foreign atoms studied.

(4) Stone-Wales defect significantly reduces the resistant force for atom insertion through the tube wall.

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